



CARNEGIE

# Annual Report of the Director Geophysical Laboratory

2801 UPTON STREET, NORTHWEST, WASHINGTON, D. C. 20008

1969-1970



Reprinted from Carnegie Institution Year Book 69 for the year July 1, 1969-June 30, 1970

Issued January 1971

Papers from the Geophysical Laboratory Carnegie Institution No. 1580 than the chromium content in the crystals from Apollo 11. The difference may be the result of a higher bulk value for the rock (0.52%  $\text{Cr}_2\text{O}_3$  in 12052 as opposed to 0.32%  $\text{Cr}_2\text{O}_3$  in 10020). Again, low  $P_{\text{O}_2}$  values of crystallization are consistent with these abnormally high chromium contents.

Magnesium, iron, and chromium were analyzed in olivines from rocks 12004 and 12022. The values are listed in Table 9B. Although somewhat richer in magnesium, the approximate values of Fo<sub>75</sub> Fa<sub>25</sub> and Fo<sub>74</sub>Fa<sub>26</sub> are not significantly different. Slight zoning in the margins of crystals is toward iron enrichment. The chromium values are very similar to those of 12052.

Bulk spectrographic analyses of the Apollo 12 rocks are listed in the Lunar Sample Information Catalog Apollo 12 (NASA-MSC-01512). The rocks are coarse grained, and spectrographic analyses of small samples may not be representative. The data for 12052, 12004, and 12022 are consistent with the olivine compositional variations, which should be chemically diagnostic of the original liquid from which the rocks crystallized. This is not true of rock 12040. The Fe/Mg ratio is close to 2.0 or higher for 12052, 12004, and 12022 but is approximately equal to 1.6 for 12040. The Cr<sub>2</sub>O<sub>8</sub> content is 0.23% in the olivines but is reported as 0.7% for the whole-rock spectrographic analysis, the highest value reported for Apollo 12 rocks.

This relative enrichment in Mg, if real, suggests higher liquidus temperatures. The olivines should reflect this as well. Electron probe measurements show the olivines in 12040 to be strongly zoned, giving an average composition of Fo<sub>50</sub>Fa<sub>50</sub>. Iron is enriched, not magnesium, as would be expected from the spectrographic analyses. The strong zoning makes an average composition meaningless, so the measured values are not listed in Table 9. The most Mg-rich core of an olivine in this rock, however, is homogeneous for a radius of approxi-

mately 30  $\mu$ m. The analysis of this core (measured by L. A. Taylor) is given in Table 9C. The composition is close to Fo<sub>0.1</sub>Fa<sub>80</sub>, still more iron rich than olivines from the other rocks.

Other checks on the discrepancy between spectrographic and electron probe analysis of the olivines were made by observation of the olivine composition as deduced by X-ray diffraction and of the compositions of chromium ulvöspinels that occur as inclusions in olivine. G. Warner (personal communication) of the NASA Lunar Receiving Laboratory reports that X-ray diffraction parameters give an average olivine composition of Fo50Fa50, entirely consistent with the present results.

The spinels in olivines have been analyzed by Haggerty and Meyer (p. 144). Clearly the spinels are the most Fe rich and Cr poor of those analyzed. The spinels in 12052 (Haggerty and Meyer, op. cit.) show this same consistency with the olivine compositions.

One can safely conclude that the olivine-spinel pairs are primary liquidus phases in the Apollo 12 rocks. They are diagnostic of the "basaltic" liquid from which they crystallized. The high chromium content signifies a low  $P_{\rm O_2}$  of crystallization, and the general composition reflects the total iron-rich composition. That Ni was not detected in these olivines is another difference from their terrestrial counterparts. Taylor, Kullerud, and Bryan (p. 241) have noted the presence of Ni in metallic phase assemblages that were entrapped in olivine crystals.

#### Apollo 12: Opaque Oxides \*

### S. E. Haggerty and H. O. A. Meyer

A comparison of the Apollo 12 samples from Oceanus Procellarium with the Apollo 11 samples from Mare Tranquillitatis reveals certain chemical similarities. Both suites show distinctive features

\*Supported in part by National Aeronautics and Space Administration contract no. 09-140-(006).

of high concentrations of refractory elements and low contents of volatile elements; these features most clearly distinguish lunar material from terrestrial or meteoritic material. One of the major differences between the two sites is the lower abundance of Ti, in both the crystalline rocks and fine material, in the Apollo 12 samples. The range in composition is 1.2 to 5.1% TiO<sub>2</sub> compared with 7 to 12% TiO<sub>2</sub> for the Apollo 11 material (Lunar Sample Preliminary Examination Team, 1970). This difference is reflected in the opaque minerals; ilmenite forms 10 to 20 modal % of the crystalline rocks of Apollo 11, whereas the concentration is 5 to 10% in Apollo 12 rocks.

The opaque minerals in the lunar material form a unique assemblage (Haggerty et al., 1970a,b; Cameron, 1970; Ramdohr and El Goresy, 1970). The major phases are ilmenite (FeTiO<sub>3</sub>), members of the chromite (FeCr<sub>2</sub>O<sub>4</sub>)—ulvöspinel (Fe<sub>2</sub>TiO<sub>4</sub>) series, members of the armalcolite series (FeTi<sub>2</sub>O<sub>5</sub>-Mg Ti<sub>2</sub>O<sub>5</sub>), troilite (FeS), and metallic iron (Fe). This assemblage reflects the highly reducing lunar environment and permits estimation of oxygen fugucity, tempera-

ture of formation, and fractionation trends during crystallization.

#### Ilmenite

Ilmenite forms between 5 and 10 modal % of the crystalline rocks examined. Optically, ilmenite is distinctly anisotropic and in oil immersion shows the deep reddish tan color that is characteristic. Extremely thin plates of ilmenite are translucent. Ilmenite grains in the crystalline rocks form (1) blocky, cuhedral to subhedral crystals: (2) thin plates parallel to {0001} with rhombohedral terminations; and (3) more rarely, coarse skeletal crystals with trapped pyroxene, troilite, and metallic iron. Electron microprobe analyses (Table 10) show ilmenite to be almost stoichiometric FeTiO<sub>3</sub>; SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, MgO, CaO, and MnO total less than 1%.

Most of the ilmenite is homogeneous, but a few individual grains of ilmenite contain lamellae of rutile,  $<10 \mu m$  thick, oriented along  $\{01\overline{1}2\}$  and lensoidal rods of a dark gray spinel phase, aligned along  $\{0001\}$ .

The secondary spinel and rutile invariably coexist within ilmenite, and they are often intimately associated,

TABLE 10. Electron Probe Analyses of Ilmenite in Samples from Apollo 12 Rocks

			i						
	12020,10	12064,6	12064,6						
	1	2	1						
SiO <sub>2</sub>		0.20	0.12						
$TiO_2$	52.3	52.8	53.1						
$Al_2O_3$	0.15	0.04	0.07						
Cr <sub>2</sub> O <sub>8</sub>	0.22	0.08	0.22						
FeO	46.9	46.8	46.7						
MgO	0.12	0.11	0.20						
CaO	0.10	0.01	0.01						
MnO	0.34	0.28	0.37						
Totals	100.1	100.3	100.8						
Number of Cations on the Basis of 3(0)									
Si		0.005)	0.0031						
Ti	0.992	0.007	0.007						
ÃÎ	$0.005 \ge 1.001$	0.001 \ 1.005	$0.002 \} 1.006$						
ĀĪ Cr	0.004	0.002	0.004						
Fe .	0.9881	0.982	0.974)						
Mg	0.004	0.004	0.007						
Ca	$0.004 \ 1.002$	0.004 0.992	0.000 \ 0.989						
Mn	0.007	0.006	0.008						

vith no clear-cut textural evidence as to their order or sequence of formation. Both spinel and a second generation of Ilmenite have been observed as oriented lamellae within the exsolved rutile, suggesting that the rutile was enriched in iron when it formed. The textures of these various intergrowths indicate that the phases are interrelated by a complex rather than a simple exsolution process, with possibly one phase triggering nucleation and growth of the other. In some instances, exsolution intergrowths are confined to ilmenite grain boundaries but contact with troilite, metallic iron, crystalline silicates, glass, or chromian ulvöspinel appears to have promoted exsolution. Such intergrowths in ilmenite have not been reported in terrestrial rocks, but chromite and rutile have been observed in ilmenite from meteorites (Buseck and Keil, 1966).

The process by which rutile and spinel are formed in ilmenite is not fully understood. In terrestrial basalts growth of rutile in ilmenite is generally the result of oxidation (Watkins and Haggerty, 1967), but Ramdohr (Year Book 63) has suggested that in meteorites reduction could also cause the generation of rutile by the breakdown of ilmenite in environments of low oxygen fugacity. The breakdown  $2\text{FeTiO}_3 \rightarrow 2\text{TiO}_2 + \text{O}_2 +$ 2Fe was not observed in lunar ilmenite. The rutile intergrowths have a texture suggesting exsolution rather than alteration, because they are oriented parallel to  $\{01\overline{1}2\}$  and have well-defined contacts that taper at the intersection of two or more lamellae. Furthermore, the orientation of spinel parallel to the basal plane is characteristic of magnetite lamellae in Imenite (Buddington and Lindsley, 1984). The fact that rutile and spinel are either crosscutting or intimately associated suggests that this is a complex. crystallographically controlled breakdown.

It is possible that both reduction and exsolution from a supersaturated host have caused the growth of these lamellae.

The sparse distribution of exsolved grains suggests a selective nonequilibrium reduction process rather than simple exsolution. Evidence of reduction in the form of reduced phases is lacking in ilmenite, however, but is present in chromium ulvöspinel from the same samples.

## Spinels

A group of new variety minerals, variously described as chromian ulvöspinel (Haggerty et al., 1970a,b), titanian chromite (Cameron, 1970), and alumian chromite (Agrell et al., 1970) were discovered in a restricted number of samples from the Apollo 11 material. These spinels are not new minerals but are compositionally distinct from terrestrial and meteoritic analogues and for purposes of comparison may be regarded either as Cr-rich titanomagnetites (e.g., 23.5% Cr<sub>2</sub>O<sub>3</sub>) or Ti-rich chromites (e.g., 20.9% TiO<sub>2</sub>). There is a restricted solid solution between ulvöspinel and chromite in terrestrial and meteoritic occurrences. Terrestrial titanomagnetites contain between 0.1 and 0.38% Cr<sub>2</sub>O<sub>3</sub> (Deer, Howie, and Zussman, 1962b; Carmichael, 1967). Chromites generally have small concentrations of TiO2, although both rutile (Ramdohr, 1963; Buseck and Keil, 1966) and ilmenite (Ramdohr, 1963; Legg, 1969) have been observed as exsolution intergrowths. Among terrestrial chromites those richest in TiO2 are usually found in basaltic lavas and contain 1.3 to 2.5% TiO<sub>2</sub> (Babkine et al., 1965; Haggerty, 1968). An unusual chromite occurrence in the Bushveld, however, has a reported TiO, content of 12.8% (Frankel, 1942). A meteoritic chromite analyzed by Buseck and Keil (1966) contains 2.9% TiO2. A complete solid solution series exists between magnetite (Fe2+Fe3+2O4) and chromite (FeCr<sub>2</sub>O<sub>4</sub>) and also between magnetite and ulvöspinel (Fe<sub>2</sub>TiO<sub>4</sub>). Although a solid solution series has not been experimentally demonstrated between Fe<sub>2</sub>TiO<sub>4</sub> and FeCr<sub>2</sub>O<sub>4</sub>, the reported analyses from Apollo 11 (Agrell *et al.*, 1970) indicate that such a series exists, supporting the suggestions of Evans and Moore (1968) and Legg (1969).

Members of the series chromite (Cr)-ulvöspinel (Usp), somewhat similar to the chromian ulvöspinels described above, occur extensively throughout the Apollo 12 samples (Haggerty and Meyer, 1970) but differ in several respects from those in Apollo 11. The Apollo 12 spinels are mineralogically distinct, fall into two well-defined compositional groups on either side of the Apollo 11 spinels along the join Fe<sub>2</sub>TiO<sub>4</sub>-FeCr<sub>2</sub>O<sub>4</sub>, show a wide variety of unusual optical properties and textures, and also show the first evidence of subsolidus reduction reactions in the lunar material.

# Optical Properties

Five optically distinct spinels have been identified in the Apollo 12 crystalline rocks (Plate 3A-D). These spinels may be divided into two groups, optically isotropic chromites and optically anisotropic chromian ulvöspinels. The isotropic group are either blue or gray in color, whereas the anisotropic group are tan, pink, or khaki in color. Estimated reflectivity values for the isotropic group are 12-15%, those for the anisotropic tan and pink minerals 18-20%, and for the khaki phase 22-25% (cf. ilmenite 20-22%). The isotropic group are harder than the anisotropic group and both are harder than ilmenite. Terrestrial and synthetic ulvöspinels and chromites are optically isotropic, but the lunar chromian ulvöspinels are consistently anisotropic. The crystalline rocks examined in this study are unshocked, and so anisotropy due to lattice distortions is unlikely. Anionic deficiencies are possible under the highly reducing lunar environment, but such defects would not be observed optically. It is therefore suggested that the chromian ulvöspinels are a new group of nonisometric phases along the join Fe<sub>2</sub>TiO<sub>4</sub>-FeCr<sub>2</sub>O<sub>4</sub> and are therefore not true spinels.

### Textures and Paragenesis

The isotropic blue and gray spinels are the earliest crystallization products and occur in olivine and pyroxene as euhedral crystals in the size range 20-100  $\mu$ m. Isotropic spinels in the groundmass are always rimmed (Plate 3A-B) by overgrowths of anisotropic spinels of the tan or pink variety and never of the khaki type; the khaki phase is anhedral and occurs in complex intergrowths with metallic iron and ilmenite (Plate 3D). The overgrowths vary in thickness from <10 to 150 µm. Contacts between core and overgrowths are generally gradational, although sharp, optically welldefined contacts are also observed. In terrestrial basalts chromite is also the first mineral to form; chromite in the groundmass is always rimmed by titanomagnetite, whereas chromite in olivine or pyroxene is unzoned (Haggerty, 1968). By contrast the Apollo 11 chromian ulvöspinels are rimmed by ilmenite (Haggerty et al., 1970a,b). In Plate 3A the paragenetic sequence for the Apollo 12 opaque minerals is illustrated; chromite forms the core of the assemblage. followed by chromian ulvöspinel, ilmenite, and finally metallic iron plus troilite (eutectoid-type intergrowth). Ilmenite overgrowths on chromite were not observed. The oxide overgrowths are interpreted as progessive zoning that has developed as a result of reaction with liquid. A consequence of this interpretation, and the paragenetic sequence, is that an early depletion of Cr and an enrichment of Fe and Ti in the liquid are indicated during crystallization.

Crystallization trends for the opaque oxides from Apollo 11 and 12 missions and for typical terrestrial basalts are summarized and contrasted in Fig. 59 in terms of the system (FeMg) O-TiO<sub>2</sub>-(CrAl)<sub>2</sub>O<sub>8</sub>.

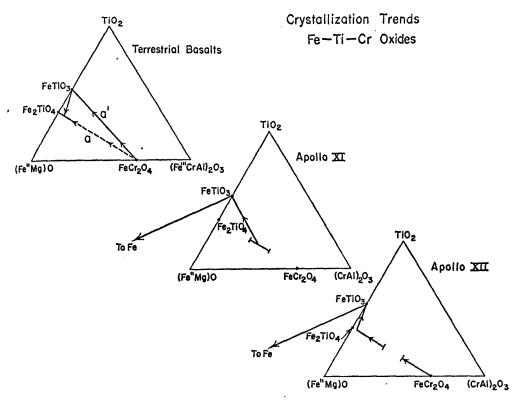


Fig. 59. Simplified crystallization trends for the Fe-Ti-Cr oxides in terrestrial basalts compared with those in rocks from the Apollo 11 and 12 lunar missions.

#### Subsolidus Reactions

Exsolution lamellae of ilmenite and minute blebs of metallic iron occur along (111) planes in chromian ulvöspinel (Plate 3E). The lamellae are tapered, pinch on intersection, and have all the oxidation-exsolution features ilmenite in titanomagnetite. The presence of metallic iron, however, is a direct indication that a process of reduction rather than oxidation has been operative. Ilmenite is commonly observed along cracks and grain boundaries in chromian ulvöspinel. Each ilmenite lamella is flanked by a gradational gray Cr-rich lamella, which is also gradational on contact with Cr ulvöspinel. The distribution of FeO, TiO<sub>2</sub>, and Cr<sub>2</sub>O<sub>8</sub> across two ilmenite lamellae is shown in Fig. 60. The ilmenite is well defined in terms of high TiO<sub>2</sub> and low Cr<sub>2</sub>O<sub>3</sub> but note the 4-5 wt % increase in chromium at the ilmenite lamellae contacts; this Cr residuum is the result of preferential migration of Fe and Ti from the spinel to form ilmenite during subsolidus reduction. It is generally accepted that  $P_{0}$ , decreases during crystallization, but whether these intergrowths formed deuterically or by some postdeuteric process is not known. On the basis of Fe-Ni ratios in metals from the Apollo 12 samples, Reid et al. (1970) have suggested that the metal is reduced from the melt as crystallization proceeds; this possibility would support a deuteric origin for the exsolved ilmenite.

#### Chemistry

Fifteen electron microprobe analyses on the five Fe-Ti-Cr oxides (gray, blue, tan, pink, khaki) have been carried out

# APOLLO XII

Exsolved Ilmenite in Cr-Ulvöspinel Analyses: I  $\mu$ m intervals 12040-4

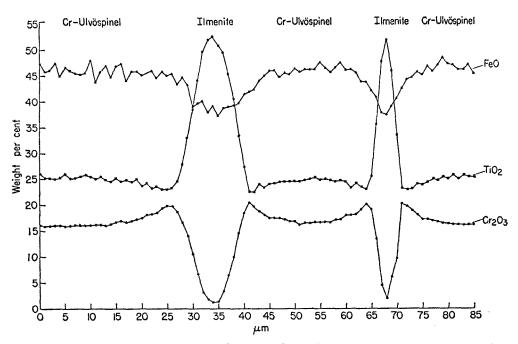


Fig. 60. Single traverse of uncorrected electron probe analyses at 1-μm intervals across exsolved lamellae of ilmenite in chromium ulvöspinel.

on four polished thin sections (12020,10; 12040,4; 12052,6; 12064,6) of unshocked microgabbros. The data are presented in Tables 11 and 12 and Fig. 61. Data on coexisting ilmenite are also presented (Table 10).

The spinel analyses fall into two separate and distinct compositional groups along the join Fe<sub>2</sub>TiO<sub>4</sub> (Usp)-FeCr<sub>2</sub>O<sub>4</sub>(Cr) in the ternary system (FeMg)O-TiO<sub>2</sub>-(CrAl)<sub>2</sub>O<sub>3</sub> (Fig. 62). The isotropic (gray and blue) spinels are Cr rich (Usp<sub>9</sub>Cr<sub>91</sub>-Usp<sub>25</sub>Cr<sub>75</sub>), whereas the anisotropic (tan, pink, khaki) chromian ulvöspinels are richer in Fe and Ti (Usp<sub>74</sub>Cr<sub>26</sub>-Usp<sub>90</sub>Cr<sub>10</sub>). These oxides are in direct contrast to spinels from the Apollo 11 samples (Usp<sub>45</sub>Cr<sub>55</sub>-Usp<sub>93</sub>Cr<sub>37</sub>). The distribution and separation of the

Apollo 12 analyses, on either side of the Apollo 11 spinels, suggest that a miscibility gap may be present along the join ulvöspinel-chromite. The Apollo 11 samples fall within this gap. If a solvus is present it would suggest either that the Apollo 11 spinels crystallized metastably or that these rocks were quenched from a higher temperature than those of Apollo 12. The miscibility gap extends from Usp<sub>42</sub>Cr<sub>58</sub>-Usp<sub>66</sub>Cr<sub>34</sub>, although further work on other samples may narrow the extent of the chromite-rich limb.

The gradational overgrowths of chromian ulvöspinel on chromite, discussed above, are interpreted as continuous reaction with liquid during slow crystallization; such overgrowths provide further evidence for the suggested solvus.

TABLE	11.	Electron	Probe	Analyses	of	Chromian	Ulvöspinels
				m Apollo			<del>.</del>

Sample Color	12040,4 Tan	12040,4 Tan	12040,4 Pink	12064,6 Pink	12020,10 Tan	12064,6 Tan	12064,6 Khaki
SiO <sub>2</sub>			• • •	0.19		0.33	0.17
TiO <sub>2</sub>	22.8	23.8	25.6	28.0	28.7	31.1	32.2
$Al_2O_3$	5.06	4.88	3.84	2.64	2.67	2.66	2.32
Cr <sub>2</sub> O <sub>3</sub>	17.9	17.5	13.3	9.34	8.61	3.64	1.50
FeO	51.9	51.8	<b>5</b> 5.0	58.6	58.8	61.8	62.9
MgO 、	2.44	2.86	2.31	0,21	0.41	0.17	0.13
CaO	0.00	0.01	0.02	< 0.01	0.05	< 0.01	< 0.01
MnO	0.53	0.52	0.50	0.27	0.30	0.16	0.29
Totals	100.6	101.4	100.6	99.3	99.5	99.9	99.5
		Number o	f Cations or	the Basis	of 32(O)		
Si	•••	• • •	• • •	0.055	• • •	0.097	0.049
Ti	4.895	5.068	5.555	6.250	6.382	6.895	7.200
Al	1.704	1.625	1.305	0.924	0.931	0.926	0.813
Cr	4.053	3,906	3.032	2.192	2.015	0.849	0.352
Fe	12.409	12.235	13.267	14.555	14.544	15.239	15.626
Mg	1.037	1.205	0.991	0.092	0.182	0.075	0.059
Ca	0.000	0.004	0.007	0.000	0.015	0.000	0.000
$\mathbf{M}\mathbf{n}$	0.128	0.124	0.121	0.068	0.075	0.039	0.072
Totals	24.226	24.167	24.278	24.136	24.144	24.120	24.171

<sup>\*</sup>Analyses are listed in increasing concentrations of TiO<sub>2</sub>. These spinels are optically anisotropic and are contrasted from those in Table 12, which are optically isotropic.

Uncorrected microprobe analyses for FeO,  $Cr_2O_3$ , and  $TiO_2$ , taken at 1- $\mu$ m intervals, across an ilmenite+Cr-Usp (pink)+Cr-Usp (tan)+chromite (gray) assemblage are illustrated in Fig. 62. Units of five or ten analyses were aver-

aged for points across the gradational contact, and typical values for MgO and Al<sub>2</sub>O<sub>3</sub> were used in the final microprobe corrections. These data are plotted in Fig. 63 as mean values for nine gradational-contact analyses. In spite of the

TABLE 12. Electron Probe Analyses of Chrome Spinels in Samples from Apollo 12 Rocks\*

Sample Color	12052,6 Gray	12052,6 Gray	12052,6 Gray	12020,10 Gray	12052,6 Gray	12020,10 Blue	12040, <b>4</b> Gray	12064, <b>6</b> Gray	
SiO <sub>2</sub>	0.12	0.14	0.14		0.09			0.26	
$TiO_2$	4.22	4.31	4.43	4.72	5.54	6.89	7.39	9.14	
$Al_2O_3$	12.02	11.83	11.86	12.3	11.88ء	13.5	12.2	12.5	
$\mathrm{Cr_2O_3}$	48.30	48.84	48.90	45.0	45.99	42.2	40.4	37.9	
${ m FeO}$	26.02	<b>2</b> 6.87	25.95	31.2	29.41	30.9	35.2	33.8	
$_{ m MgO}$	7.43	7.74	7.43	4.94	6.46	6.93	4.59	5.29	
CaO	0.04	0.04	0.01	0.10	0.06	0.01	0.06	0.01	
$\mathbf{MnO}$	0.75	0.76	_0.76	0.17	0.64	0.23	0.72	0.21	
Totals	98.9	100.5	99.4	98.4	100.0	100.7	100.6	99.1	
Number of Cations on the Basis of 32(0)									
Si	0.032	0.037	0.038		0.025	• • •		0.070	
Ti	0.857	0.862	0.893	0.980	1.178	1.375	1.513	1.870	
Al	3.822	3.708	3.747	4.007	3.769	4.224	3.914	4.003	
$\mathbf{Cr}$	10.298	10.269	10.365	9.812	9.784	8.840	8.702	8.152	
$\mathbf{Fe}$	5.869	5.977	5.818	7.211	6.617	6.860	8.004	7.688	
Mg	2.984	3.067	2.968	2.033	2.591	2.740	1.862	2.148	
Ca	0.011	0.011	0.004	0.029	0.017	0.003	0.018	0.004	
$\mathbf{M}\mathbf{n}$	0.171	0.171	0.172	0.040	-0.145	0.051	0.166	0.049	
Totals	24.044	24.102	24.005	24.112	24.126	24.093	24.179	23.986	

<sup>\*</sup> Analyses are listed in increasing concentrations of TiO2.

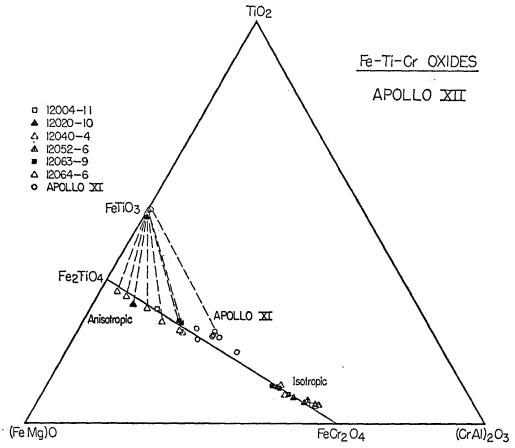


Fig. 61. (FeMg)O-TiO<sub>2</sub>-(CrAl)<sub>2</sub>O<sub>3</sub> plot of spinel analyses from Apollo 12 samples. Full and open squares are from Table 16 (Taylor, Kullerud, and Bryan, p. 243). Apollo 11 results are shown for comparison; data drawn from Agrell et al., 1970.

observed optical gradation, it is noted that none of these data points falls within the miscibility gap.

The presence of approximately 90% of the Fe<sub>2</sub>TiO<sub>4</sub> molecule in the khaki chromian ulvöspinel (12064,6) defines this phase as being the most Fe<sub>2</sub>TiO<sub>4</sub>-rich mineral yet found in nature. Terrestrial ulvöspinels, possibly comparable in Fe<sub>2</sub>TiO<sub>4</sub> to the above material, may occur in ulvöspinel exsolution lamella within magnetite. Analyzed terrestrial material (usually titaniferous magnetites) contains less than 50% of the Fe<sub>2</sub>TiO<sub>4</sub> molecule (Deer, Howie, and Zussman, 1962b, p. 74), however, whereas in the Apollo 12 lunar ulvöspinels 60% is the minimum value.

Recalculations of the analyses in Tables 11 and 12 into possible spinel molecules indicates the presence of excess Fe2+. In order to retain charge balance on the basis of 32 oxygen atoms some of this excess Fe2+ must be considered as Fe3+, thus allowing the formation of Fe<sup>2+</sup>Fe<sup>3+</sup>O<sub>4</sub>-magnetite. In general the amount of the magnetite molecule is not greater than 4%, corresponding roughly to a maximum of 4% by weight of Fe<sub>2</sub>O<sub>3</sub> in the original analyses. The presence of this small amount of Fe<sub>2</sub>O<sub>3</sub> when added to the (Al,Cr)<sub>2</sub>O<sub>8</sub> corner of Fig. 61 allows the individual ulvöspinel analyses to move closer to or onto the join Fe2TiO4-Fe Cr2O4.

# APOLLO XII

Analyses : I  $\mu$ m intervals 12020-10

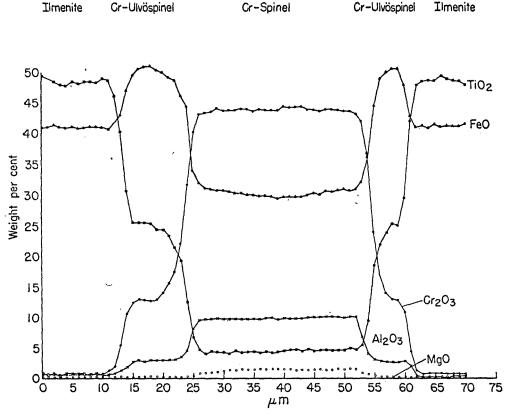


Fig. 62. Traverse of uncorrected electron probe analyses at 1-μm intervals across chrome spinel, chromium ulvöspinel, ilmenite complex. Chrome spinel forms the core of the assemblage with gradational and consecutive overgrowths of chromium ulvöspinel and ilmenite.

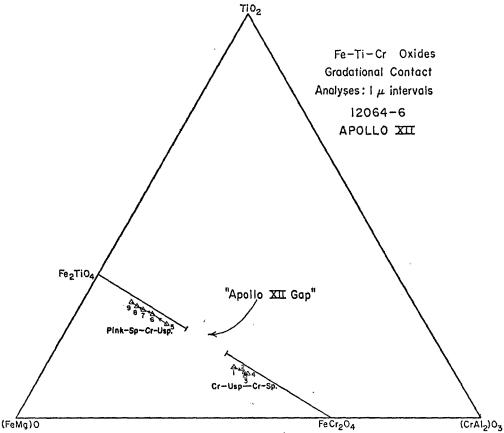


Fig. 63. Corrected electron probe analyses obtained from data presented in Fig. 62. The coordinates of this plot are similar to that of Fig. 61. Contacts between phases are optically gradational, but compositionally a distinct miscibility gap is present along the join ulvöspinel-chromite.

The abundance of Fe<sup>3+</sup> in lunar whole-rock analyses is small, and because of the presence of free metallic iron, has been considered suspect. Taylor (1964), however, in studying the system FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> at 1300°C, has shown the possible presence of ulvöspinel containing some magnetite in equilibrium with wüstite and metallic iron. Undoubtedly these relationships will be affected by the addition of Cr, Mg, and Al, but at present no experimental data applicable to this discussion are available.

INVESTIGATIONS OF APOLLO 12 SAMPLES L. A. Taylor, G. Kullerud, and W. B. Bryan

The lunar samples provide an unprecedented opportunity to study phase relations in rocks crystallized under highly reducing conditions. The lunar rocks differ from meteorites both in bulk composition and in the nature and composition of individual mineral phases. Because in effect the rocks represent a natural experiment in a different portion of the complex sulfide-oxide-metal-silicate "system" than has previously been available for study, our initial investigations were designed mainly to define mineralogical and chemical relationships on which to base detailed experiments in portions of the natural system.

We have determined major and minor element concentrations in coexisting metal, sulfide, oxide, and silicate phases.\*

\*The microprobe used for these analyses was purchased with the support of NSF grant GP 4384. Some of the data were reported by Taylor, Kullerud, and Bryan (1970).